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DRD NO. SE5
DRL NO. 203

LASER-ASSISTED SOLAR CELL METALLIZATION PROCESSING

S. Dutta

Quarterly Report for the Period December 13, 1983 to March 12, 1984

Jet Propulsion Laboratory
Contract No. 956615

April 3, 1984

Westinghouse R&D Center
1310 Beulah Road
Pittsburgh. Pennsylvania 15235

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by the United States Department of Energy through an agreement with the National Aeronautics and Space Administration.

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1. SUMMARY

The aim of this contract is to investigate, develop, and characterize laser-assisted processing techniques utilized to produce the fine-line, thin-metal grid structures that are required to fabricate high-efficiency solar cells. The tasks comprising these investigations are summarized in the milestone chart in Figure 1.

During the first quarter of this contract, a comprehensive literature search was carried out on the various state-of-the-art laser-assisted techniques for metal deposition, including laser chemical vapor deposition and laser photolysis of organometallics, as well as laser-enhanced electroplating. A compact system for the experiments involving laser-assisted photolysis of gas-phase compounds was designed and constructed. Initial experiments on laser-enhanced electroplating yielded very promising results with linewidths as narrow as 25 μm and plating speeds as high as 12 μm/sec being achieved.

The work performed in the second quarter is detailed in this report. Metal deposition experiments have been carried out utilizing laser-assisted pyrolysis of a variety of metal-bearing polymer films and metallo-organic inks spun onto silicon substrates. Laser decomposition of spun-on silver neodecanoate ink obtained from Purdue University has yielded very promising results. Solar cell comb metallization patterns have been written using this technique, each pattern being written in a fraction of a second. Electrical characterization of the metal deposits and measurement of the solar cell characteristics obtained using this metallization scheme will be carried out. Preliminary experiments involving the laser-assisted deposition of titanium and tin are planned. An economic evaluation of the two processes -- pyrolytic decomposition of spun-on films and photolytic decomposition of organometallic vapors

MILESTONE CHART
JPL CONTRACT 956615

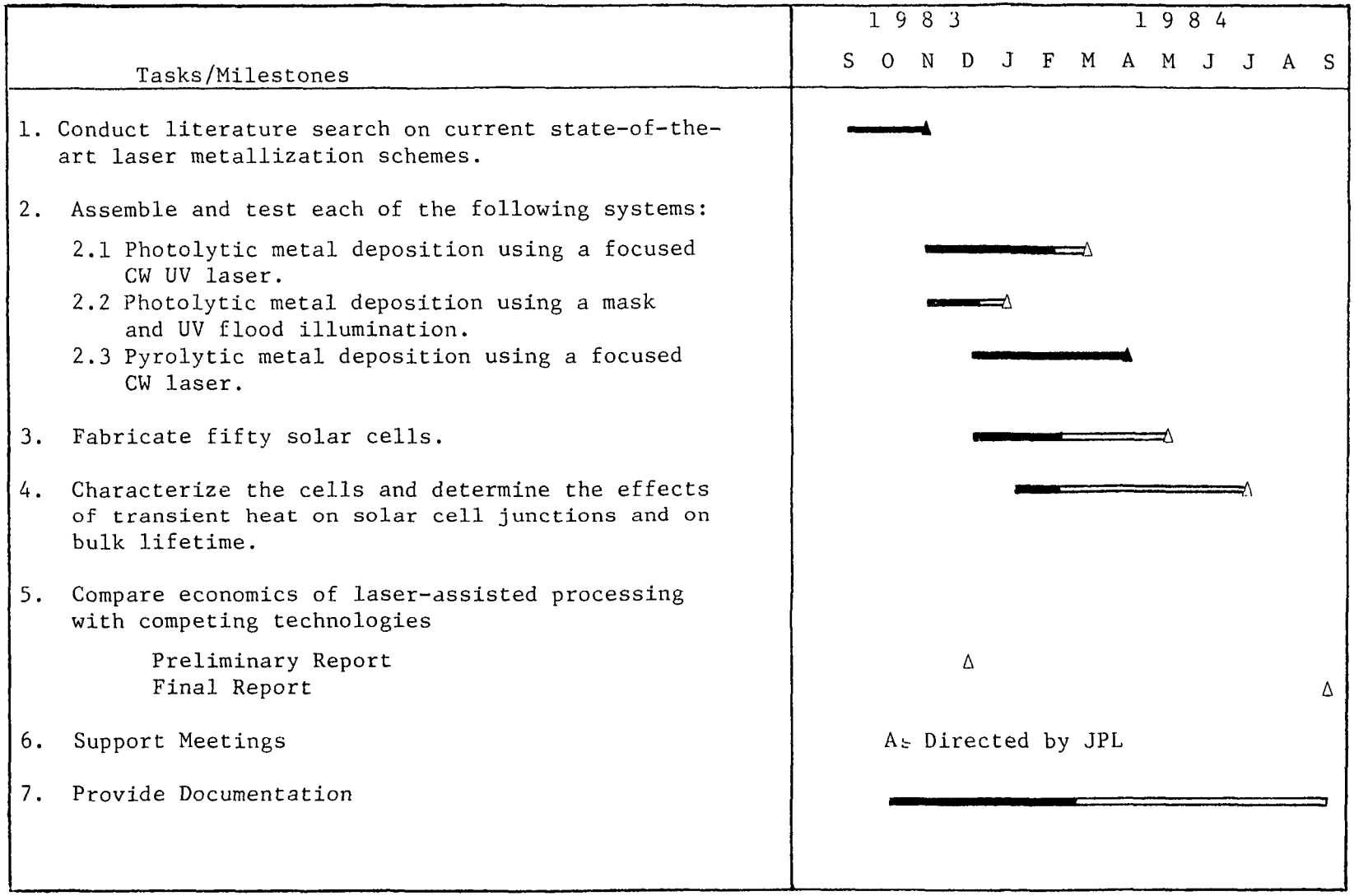

Figure 1. Milestone Chart

-- will then be performed. Progress on this project was summarized at the 23rd Project Integration Meeting on March 14 and 15 at Pasadena.

2. RESULTS AND DISCUSSION

2.1 Laser-Assisted Pyrolysis

Deposition of metals by laser-assisted pyrolysis of a variety of metallo-organic inks and metal-bearing polymer solutions spun as films onto silicon wafers has been carried out. The films that have been laser-exposed include gold and palladium bearing polymers from Emulsitone Company, tantalum, chromium, and molybdenum metallo-organic compounds from Engelhardt Corporation, and a silver metallo-organic ink, silver neodecanoate, synthesized by Professors Robert and Geraldine Vest of Purdue University. The films used in these experiments are listed in Table 1. Laser decomposition of these films has been carried out using a focused argon-ion laser and x-y scanning mirrors as shown in Figure 2.

The commercial films from Emulsitone and Engelhardt did not spin on uniformly or decompose cleanly into metallic-looking deposits upon exposure to the laser. The silver neodecanoate metallo-organic ink from Purdue University, however, has yielded very promising results. It spins on very uniformly and decomposes into bright silver deposits at laser power densities as low as 1.5×10^4 W/cm^2, corresponding to a laser power of 1 W and a spot size of ~ 94 μm, and beam scan rates as high as 50 cm/sec. The high-magnification Nomarski photomicrograph shown in Figure 3 clearly demonstrates the high-quality, dense, fine-grain nature of the laser-decomposed silver. Figure 4 shows the dependence of the deposited linewidth on laser power and spin speed. The linewidth initially increases with laser power, as expected, as the portion of the Gaussian beam above the threshold power for film decomposition increases. This effect saturates when the linewidth becomes equal to the laser spot size. Increasing the spin speed decreases the film thickness, and consequently the laser power required

Table 1

LIST OF SPIN-ON LIQUIDS DECOMPOSED BY LASER PYROLYSIS

Metal	Compound	Supplier
Ag	Silver neodecanate	Professors R. and G. Vest, Purdue University
Au	Gold-bearing polymer, composition unknown	Emulsitone Company
Pd	Palladium-bearing polymer, composltion unknown	Emulsitone Company
Ta	Tantalum metallo-organic, composition unknown	Engelhardt Corporation
Mo	Molybdenum metallo-organic, composition unknown	Engelhardt Corporation
Cr	Chromium metallo-organic, composition unknown	Engelhardt Corporation

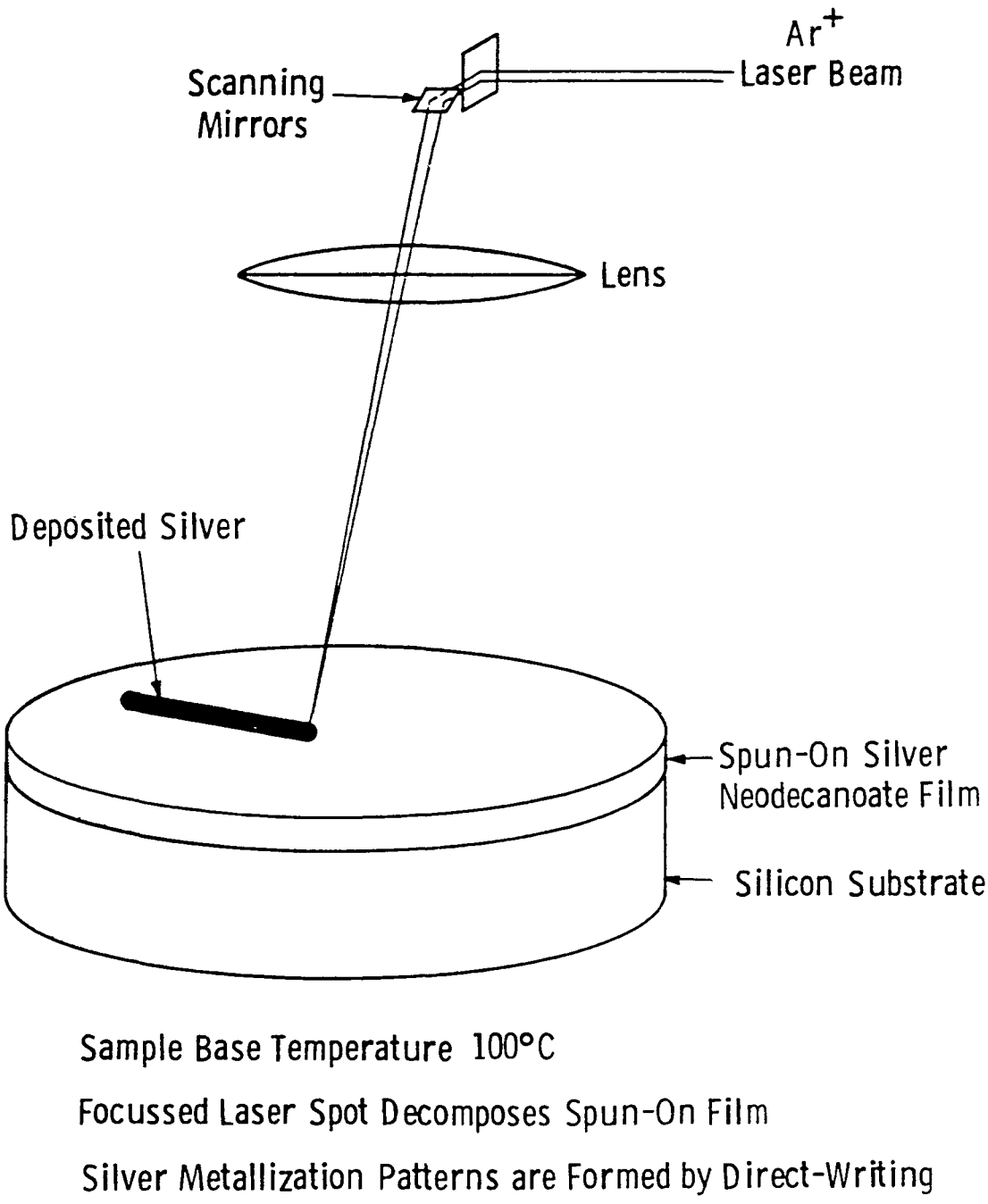

Figure 2. Schematic of experimental set-up for laser pyrolysis of spun-on metallo-organic films.

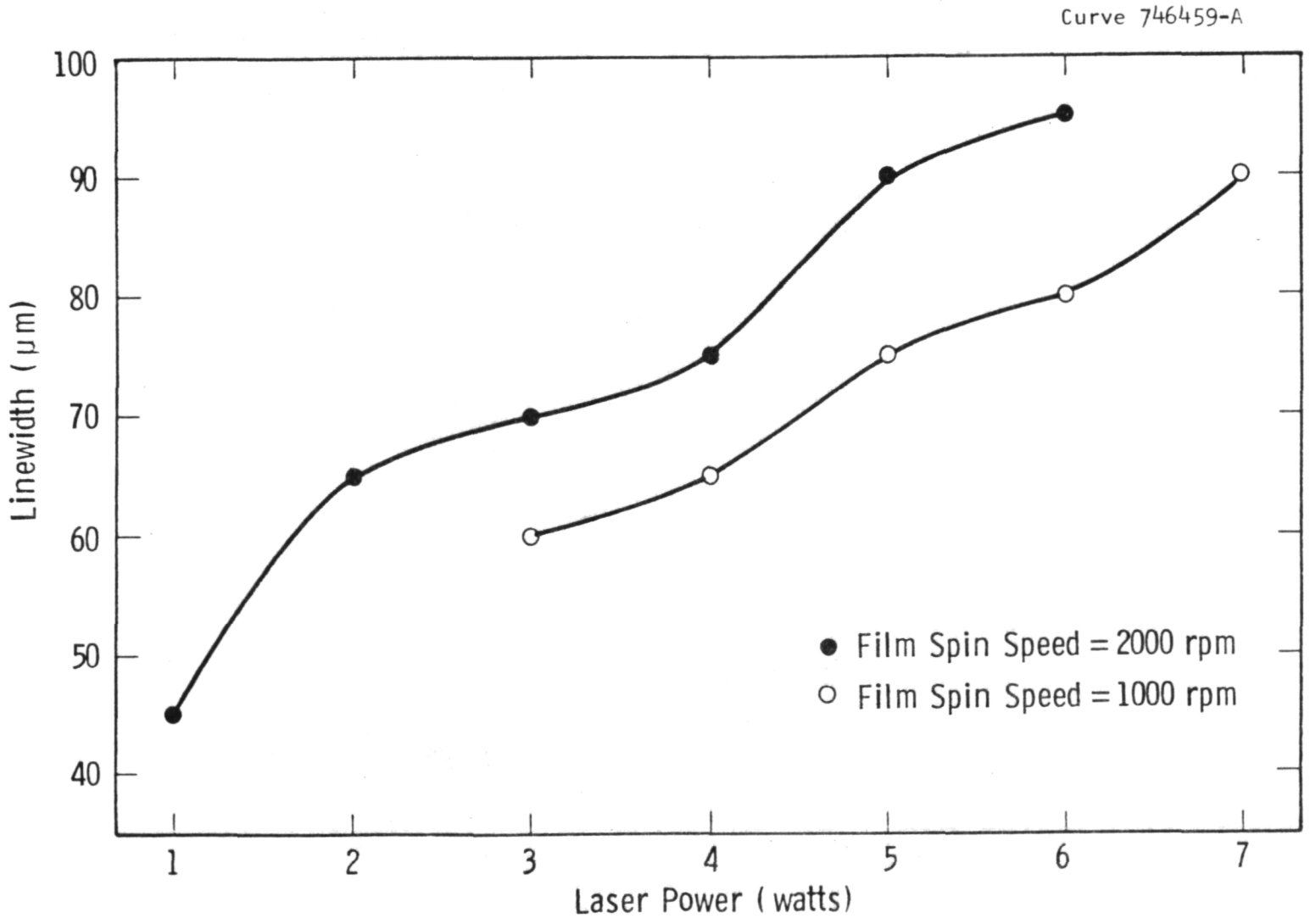

Figure 3. Dependence of laser-deposited linewidth on laser power and spin speed.

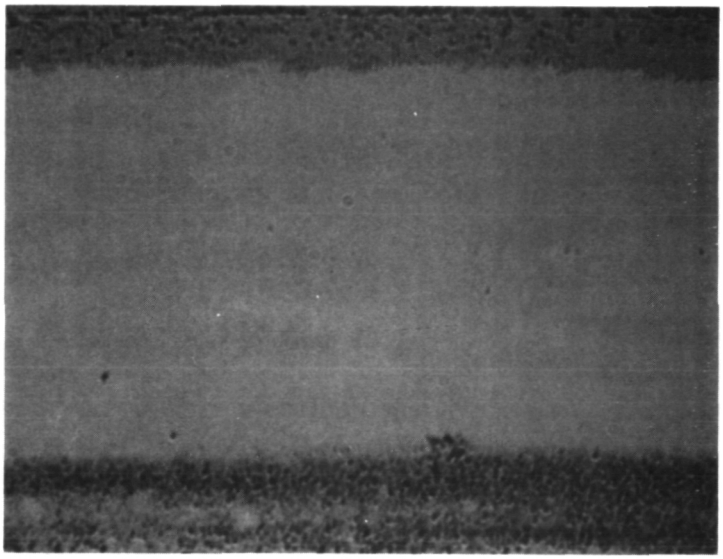

Figure 4. 1000X Nomarski micrograph of silver deposited at a laser power of 6W.

for decomposition. It should be emphasized, however, that much finer linewidths may be obtained by going to lower laser powers or a tighter focusing system.

In the initial experiments involving silver neodecanoate, the substrate was held at room temperature during the laser decomposition process. It has been found that the deposited silver does not adhere very well under these deposition conditions, being washed away with the rest of the film during the subsequent acetone rinse. Subsequent experiments have been carried out with the substrate being heated gradually to 100°C prior to laser processing. The substrate temperature is then held at 100°C during the laser decomposition. Adhesion of the deposited silver has been found to improve considerably under these conditions. The deposited silver does not, however, pass the "Scotch-tape" test of adhesion yet. Experiments involving post-deposition sintering are being carried out to improve adhesion. Laser decomposition is also being performed with the substrate held at temperatures ranging from 0-100°C to see which temperature condition yields the most adherent deposits.

Ten solar cell comb metallization patterns have been directly laser written on a two-inch silicon wafer with silver neodecanoate spun onto its surface, as shown in Figure 5. Each line was written using a single laser scan, and the contact pads were written using x-y raster scans that overlapped by 50%. Laser powers ranging from 1 to 7 W were used, and the substrate was gradually heated to and held at 100°C. Scan velocities of 20 cm/sec were used, resulting in a total time of 0.7 sec for each comb pattern. Such rapid writing speeds enable this technique to appear economically attractive. Solar cell fabrication is being carried out using this metallization technique.

2.2 Laser-Assisted Photolysis

The gas-fill and pumping station for the laser photolysis of gas-phase organometallics has been set up inside a fume hood, connected

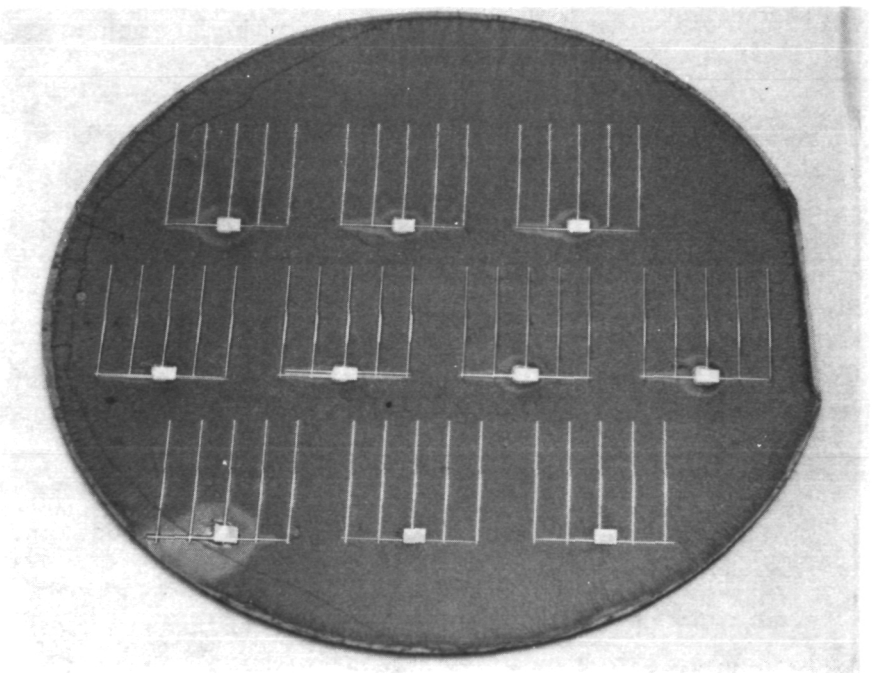

Figure 5. Laser-written solar cell metallization patterns using spin-on silver neodecanoate.

to the various gas supplies, and fitted with a heater assembly and thermocouple gauges. A schematic of this station is shown in Figure 6. As one of the compounds to be photolyzed is titanium tetrachloride, which corrodes stainless steel, an additional sample chamber has been constructed from carbon steel, which is more corrosion resistant. Sample holders, fitted within the sample chambers and designed to vary the substrate position relative to the chamber window, have been constructed. There has been a slight delay caused by the replacement of the fume hood exhaust system. Preliminary experiments involving the laser-assisted deposition of tin and titanium will be carried out as soon as possible, using the experimental set-up depicted schematically in Figure 7. An economic evaluation of this technique can then be performed.

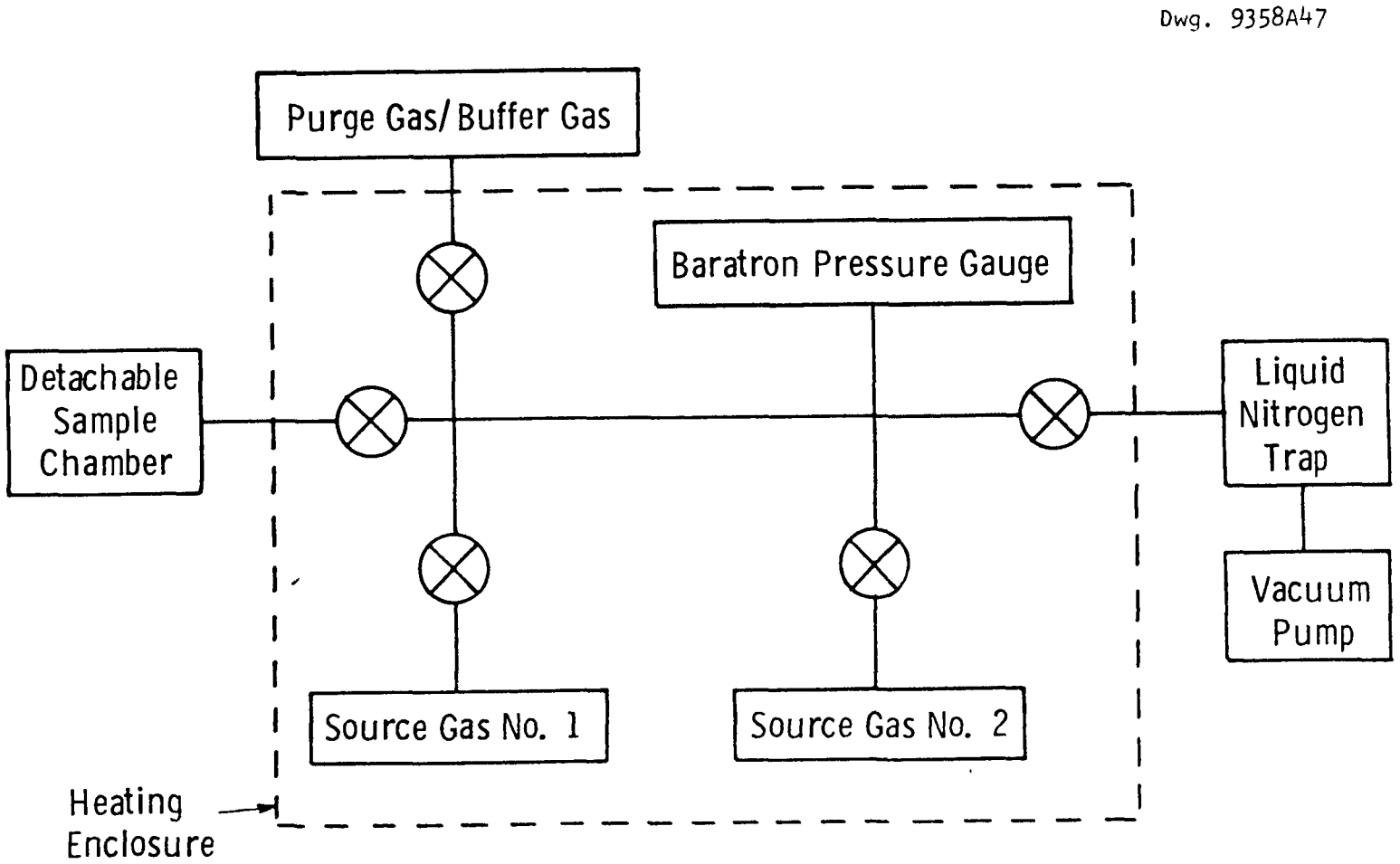

Figure 6. Schematic of gas-fill and pumping station for laser-assisted photolysis

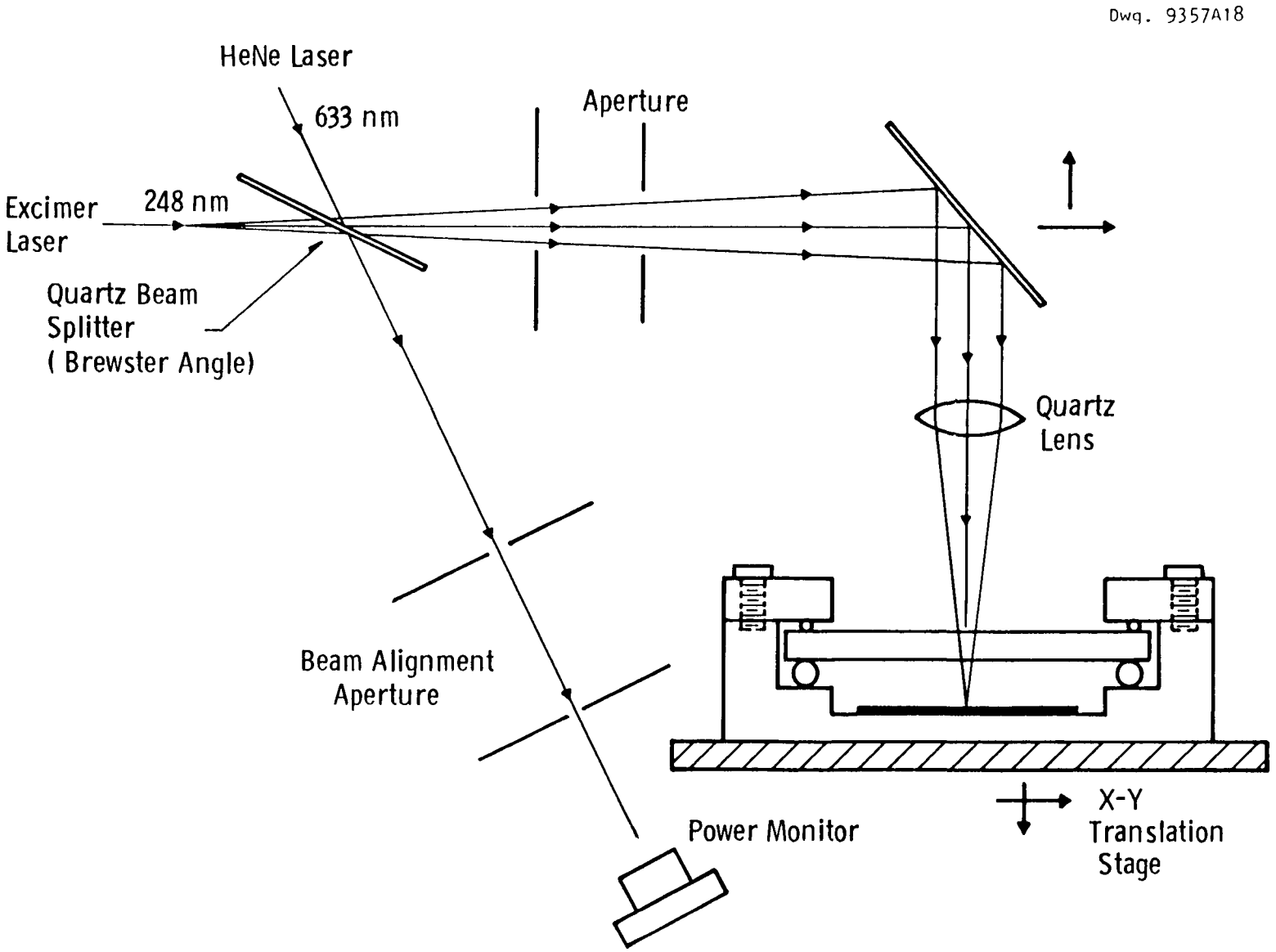

Figure 7. Schematic of experimental set-up for laser-assisted photolysis.

3. CONCLUSIONS AND RECOMMENDATIONS

The laser-assisted pyrolysis of spun-on silver neodecanoate films appears to be an extremely promising technique. Solar cell comb metallization patterns have been directly written in times as short as 0.7 sec per cell, making it an economically attractive technique. The optical appearance of the deposited silver indicates that it is dense, high-quality material. Adhesion has been improved by substrate heating techniques, but there are still problems which are being addressed. Contact and sheet resistance measurements and solar cell characterization need to be performed once the adhesion has been sufficiently improved. A SAMICS evaluation of this technique can then be made.

Laser-assisted photolysis experiments using gas-phase compounds of tin and titanium will shortly be carried out. A decision on whether to continue with this technique will be made based on the preliminary data.

4. PROJECTION OF ACTIVITIES FOR THIRD QUARTER

A SAMICS economic evaluation of solar cells metallized by laser pyrolysis of silver neodecanoate will be performed. Electrical characterization of the deposited metal and solar cell measurements to determine the effect of transient heating on junctions and bulk lifetime will be carried out. The first experiments on laser-assisted photolysis will be performed, and a decision made on whether to progress further with this technique for solar cell metallization.

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